## Detailed Experimental

**Apparatus.** An apparatus for delivering known concentrations of organic vapors was constructed from solvent bubblers, solenoids, and mass flow controllers. Flow switching and data acquisition were computer controlled with LabVIEW software.

**Fabrication of Substrates.** Glass substrates for detector fabrication were prepared by evaporating 300 Å of chromium followed by 500 Å of gold onto microscope slides masked with a 3 mm strip of drafting tape down the center of the long axis. These slides were then cut down their short axis to give 15 smaller pieces from each slide.

**Block Copolymer Synthesis.** Polymers were prepared according to the procedure in reference 19. The mass ratio of monomer to catalyst was held constant (21:1) and the composition of the monomers was varied from 100% A to 100% B with five equally spaced compositions in between.

**Fabrication of Sensors.** Individual sensor elements for PMMA (poly (methyl methacrylate)) and PVC (poly (vinyl chloride)) detectors were prepared by spin coating films from terahydrofuran solutions onto the glass substrates. The electrodes and backs of the slides were cleaned with solvent prior to using the detectors. Five replicates of each detector were made for each experiment. Poly (styrene) (PS) detectors were prepared from benzene solutions on surface mount universal boards (surfboards, part 6012 from Capital Advanced Technologies) by dip coating. Poly (vinyl acetate) (PVA) sensors were prepared by spray coating (Iwata HP-BC airbrush) films from terahydrofuran onto glass substrates.

**Experiments.** Detectors were exposed to eight different solvents: methanol, ethanol, acetone, ethyl acetate, terahydrofuran, chloroform (methylene chloride in the case of the detectors formed from copolymers), toluene, and hexane. All exposures were adjusted to deliver the analyte at a concentration that was equal to 5% of the analyte's vapor pressure at room temperature. PVA- and PVC-based sensors were exposed 15 times to each solvent. Copolymers were exposed 20 times and the mean response over all exposures was reported.

**Measurements.** Detector resistance measurements as a function of time were recorded before, during, and after solvent exposure using a Keithley model 2002 multimeter attached to a Keithley model 7001 channel switcher. The average steady state dc resistance response of the composite was used to determine the differential resistance change of the detector in the presence of an analyte. Dividing this value by the baseline resistance yielded the relative differential resistance, $\Delta R/R$, which was the key quantity used to determine the response of a given composition of sensor to an analyte.

**Data analysis.** Detector responses to various solvents were analyzed through the use of the Fisher linear discriminant method. This method provides a measure of the resolving power of a given sensor array for the set of solvents. The result is a matrix of resolution factors describing the ability of the array to distinguish between pairs of solvents.

## Detailed PVA resolution factors

Arrays of PVA with different numbers of sensors (5, 4,and 2) were examined for their ability to discriminate between various analytes. More detectors led to an increase in resolution factors. The magnitude of the effect depended, however, on the specific detector set and the analytes being resolved.

Resolution factors for a 5 sensor array with PVA and PVA with DGD, GTA, CP70, TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 11.0 | 23.7 | 14.4 | 60.8 | 13.2 | 21.1 | 23.9 |
| toluene | | 17.8 | 9.0 | 35.5 | 9.4 | 12.3 | 15.9 |
| chloroform | | | 9.0 | 8.6 | 7.7 | 9.4 | 10.8 |
| THF | | | | 13.6 | 1.8 | 7.5 | 11.9 |
| acetone | | | | | 11.6 | 32.8 | 40.9 |
| ethyl acetate | | | | | | 8.1 | 12.7 |
| ethanol | | | | | | | 6.4 |

Resolution factors for a 4 sensor array with PVA with DGD, GTA, CP70, TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 10.6 | 20.6 | 14.3 | 60.8 | 13.0 | 19.6 | 23.0 |
| toluene | | 14.2 | 8.9 | 34.3 | 9.0 | 9.2 | 11.3 |
| chloroform | | | 8.4 | 8.3 | 6.5 | 9.4 | 9.1 |
| THF | | | | 12.9 | 1.7 | 5.0 | 7.1 |
| acetone | | | | | 9.5 | 32.7 | 36.7 |
| ethyl acetate | | | | | | 7.0 | 8.9 |
| ethanol | | | | | | | 4.5 |

Resolution factors for a 4 sensor array with PVA and PVA with GTA, CP70, TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 3.8 | 23.6 | 12.1 | 28.7 | 12.7 | 17.0 | 17.0 |
| toluene | | 17.3 | 7.7 | 22.4 | 8.9 | 11.8 | 15.7 |
| chloroform | | | 8.6 | 4.9 | 7.3 | 7.9 | 8.8 |
| THF | | | | 13.4 | 1.8 | 4.3 | 9.4 |
| acetone | | | | | 11.5 | 13.8 | 13.2 |
| ethyl acetate | | | | | | 4.6 | 10.6 |
| ethanol | | | | | | | 6.4 |

Resolution factors for a 4 sensor array with PVA and PVA with DGD, CP70, TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 9.9 | 21.0 | 14.1 | 56.0 | 13.1 | 20.3 | 23.8 |
| toluene | | 16.2 | 8.9 | 34.7 | 9.4 | 11.9 | 15.9 |
| chloroform | | | 8.7 | 8.6 | 7.6 | 8.9 | 10.2 |
| THF | | | | 13.5 | 1.8 | 7.5 | 11.9 |
| acetone | | | | | 11.4 | 31.8 | 40.7 |
| ethyl acetate | | | | | | 7.8 | 12.4 |
| ethanol | | | | | | | 6.4 |

Resolution factors for a 4 sensor array with PVA and PVA with DGD, GTA, TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 8.7 | 14.9 | 10.3 | 47.0 | 11.5 | 18.1 | 21.9 |
| toluene | | 13.7 | 6.0 | 26.9 | 7.9 | 9.8 | 15.8 |
| chloroform | | | 8.0 | 6.5 | 7.5 | 8.6 | 10.8 |
| THF | | | | 10.4 | 1.5 | 7.5 | 11.9 |
| acetone | | | | | 9.8 | 29.8 | 35.3 |
| ethyl acetate | | | | | | 7.6 | 12.7 |
| ethanol | | | | | | | 6.3 |

Resolution factors for a 4 sensor array with PVA and PVA with DGD, GTA, CP70

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 10.9 | 23.7 | 14.1 | 59.2 | 12.7 | 20.9 | 23.4 |
| toluene | | 17.7 | 8.8 | 35.1 | 9.3 | 12.2 | 15.2 |
| chloroform | | | 9.0 | 7.8 | 7.7 | 9.3 | 10.8 |
| THF | | | | 12.2 | 1.6 | 7.2 | 11.8 |
| acetone | | | | | 10.6 | 32.6 | 40.0 |
| ethyl acetate | | | | | | 8.0 | 12.6 |
| ethanol | | | | | | | 6.4 |

Resolution factors for a 2 sensor array with PVA and PVA with DGD

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 7.4 | 13.8 | 9.8 | 42.3 | 11.4 | 16.8 | 20.8 |
| toluene | | 12.1 | 5.8 | 23.9 | 7.8 | 9.3 | 14.2 |
| chloroform | | | 7.8 | 5.7 | 7.3 | 8.3 | 10.1 |
| THF | | | | 8.7 | 1.4 | 7.2 | 11.8 |
| acetone | | | | | 8.9 | 29.0 | 35.0 |
| ethyl acetate | | | | | | 7.4 | 12.1 |
| ethanol | | | | | | | 6.2 |

Resolution factors for a 2 sensor array with PVA and PVA with GTA

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 0.9 | 12.2 | 5.1 | 19.6 | 7.7 | 10.8 | 15.9 |
| toluene | | 11.2 | 4.4 | 16.9 | 6.6 | 9.4 | 14.7 |
| chloroform | | | 5.5 | 1.4 | 5.4 | 1.7 | 4.9 |
| THF | | | | 8.1 | 1.0 | 4.2 | 9.3 |
| acetone | | | | | 9.3 | 3.7 | 4.3 |
| ethyl acetate | | | | | | 3.9 | 9.7 |
| ethanol | | | | | | | 6.2 |

Resolution factors for a 2 sensor array with PVA and PVA with CP70

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 2.0 | 20.9 | 9.9 | 25.2 | 11.5 | 15.1 | 16.9 |
| toluene | | 15.5 | 6.5 | 19.7 | 8.3 | 11.2 | 14.9 |
| chloroform | | | 7.6 | 3.6 | 6.5 | 5.9 | 4.7 |
| THF | | | | 10.5 | 1.5 | 4.2 | 9.3 |
| acetone | | | | | 10.1 | 9.1 | 6.9 |
| ethyl acetate | | | | | | 4.1 | 9.7 |
| ethanol | | | | | | | 6.4 |

Resolution factors for a 2 sensor array with PVA and PVA with TCP

| | Toluene | chloroform | THF | acetone | ethyl acetate | ethanol | methanol |
|---|---|---|---|---|---|---|---|
| hexane | 2.3 | 12.3 | 7.2 | 18.6 | 7.9 | 10.9 | 16.1 |
| toluene | | 10.5 | 4.3 | 15.0 | 5.7 | 9.3 | 15.3 |
| chloroform | | | 7.1 | 2.6 | 6.3 | 5.4 | 8.1 |
| THF | | | | 10.2 | 1.4 | 4.2 | 9.4 |
| acetone | | | | | 9.3 | 6.9 | 9.5 |
| ethyl acetate | | | | | | 4.2 | 10.3 |
| ethanol | | | | | | | 6.3 |

The pairwise odor discrimination performance of the electronic nose was evaluated using the Fisher linear discriminant algorithm. A resolution factor for any solvent pair can be obtained along any vector, $\vec{w}$, from the vector projection onto $\vec{w}$ of the distance between the cluster centroids, $d_{\vec{w}}$, divided by the sum of the projected standard deviations, $\sigma_{a,\vec{w}}$ and $\sigma_{b,\vec{w}}$, for data arising from repeated exposures for two

different analytes, *a* and *b*. The resulting numerical resolution factor along $\vec{w}$ is defined as:

$$rf = d_{ab}/\sqrt{\sigma_{a,\vec{w}}^2 + \sigma_{b,\vec{w}}^2}$$

The Fisher linear discriminant operates by searching for the vector, $\vec{w}$, such that the rf value is maximized along this optimal discriminant vector.

**Representative table of ΔR/R values for an array of PVA sensors**

This table contains all the ΔR/R * 100 response data used to determine the resolution factors presented above.

| solvent | PVA | PVA+DGD | PVA+GTA | PVA+CP70 | PVA+TCP |
|---|---|---|---|---|---|
| hexane | 0.017 | 0.184 | -0.170 | 0.003 | 0.122 |
| hexane | 0.018 | 0.195 | 0.039 | 0.021 | 0.153 |
| hexane | 0.017 | 0.189 | 0.150 | 0.023 | 0.107 |
| hexane | 0.010 | 0.116 | 0.153 | -0.003 | 0.008 |
| hexane | -0.019 | 0.120 | 0.144 | 0.026 | -0.121 |
| hexane | -0.025 | 0.112 | -0.006 | 0.017 | 0.105 |
| hexane | 0.003 | 0.183 | 0.000 | 0.014 | 0.137 |
| hexane | 0.008 | 0.159 | -0.164 | 0.027 | -0.071 |
| hexane | 0.021 | 0.203 | 0.006 | 0.022 | 0.163 |
| hexane | 0.013 | 0.149 | -0.148 | 0.033 | 0.182 |
| hexane | 0.020 | 0.312 | -0.045 | 0.023 | 0.207 |
| hexane | 0.040 | 0.324 | -0.012 | 0.012 | 0.729 |
| hexane | -0.012 | 0.145 | -0.056 | 0.026 | -0.015 |
| hexane | -0.008 | 0.293 | 0.073 | -0.008 | 0.157 |
| hexane | 0.009 | 0.191 | -0.009 | 0.022 | 0.104 |
| toluene | -0.017 | 1.398 | 0.199 | 0.045 | 0.640 |
| toluene | 0.022 | 1.320 | 0.049 | 0.063 | 0.736 |
| toluene | -0.009 | 1.296 | 0.389 | 0.064 | 0.587 |
| toluene | 0.020 | 1.267 | 0.199 | 0.049 | 0.959 |
| toluene | 0.029 | 1.241 | 0.018 | 0.057 | 0.702 |
| toluene | 0.023 | 1.276 | 0.042 | 0.053 | 0.662 |
| toluene | 0.052 | 1.623 | 0.098 | 0.018 | 1.402 |
| toluene | 0.043 | 1.169 | -0.235 | 0.057 | 0.989 |
| toluene | 0.011 | 1.153 | -0.117 | 0.058 | 0.695 |
| toluene | 0.038 | 1.202 | -0.121 | 0.032 | 0.712 |
| toluene | 0.021 | 1.301 | 0.076 | 0.068 | 0.706 |
| toluene | 0.038 | 1.080 | -0.086 | 0.090 | 0.599 |
| toluene | 0.037 | 1.386 | -0.074 | 0.046 | 0.582 |
| toluene | 0.026 | 1.192 | -0.023 | 0.084 | 0.636 |
| toluene | 0.066 | 1.438 | 0.124 | 0.079 | 1.150 |
| chloroform | 0.374 | 9.735 | 0.736 | 0.346 | 4.301 |
| chloroform | 0.355 | 7.966 | 0.618 | 0.328 | 3.606 |
| chloroform | 0.326 | 9.957 | 0.713 | 0.343 | 4.004 |
| chloroform | 0.347 | 7.841 | 0.827 | 0.319 | 3.188 |
| chloroform | 0.400 | 9.575 | 0.860 | 0.319 | 4.482 |
| chloroform | 0.370 | 9.510 | 0.760 | 0.346 | 4.199 |
| chloroform | 0.368 | 10.148 | 0.440 | 0.328 | 4.546 |
| chloroform | 0.323 | 10.556 | 0.607 | 0.353 | 5.219 |
| chloroform | 0.377 | 8.917 | 0.752 | 0.312 | 3.897 |

| | | | | | |
|---|---|---|---|---|---|
| chloroform | 0.371 | 9.978 | 0.360 | 0.359 | 4.038 |
| chloroform | 0.385 | 9.878 | 0.734 | 0.359 | 4.440 |
| chloroform | 0.347 | 9.921 | 0.792 | 0.334 | 4.427 |
| chloroform | 0.331 | 9.858 | 0.729 | 0.333 | 3.878 |
| chloroform | 0.364 | 10.109 | 0.754 | 0.322 | 4.533 |
| chloroform | 0.313 | 7.431 | 0.637 | 0.331 | 3.548 |
| tetrahydrofuran | 0.122 | 2.933 | 0.158 | 0.212 | 1.583 |
| tetrahydrofuran | 0.107 | 2.750 | 0.594 | 0.192 | 1.883 |
| tetrahydrofuran | 0.130 | 2.163 | 0.437 | 0.180 | 1.261 |
| tetrahydrofuran | 0.156 | 2.842 | 0.341 | 0.205 | 1.487 |
| tetrahydrofuran | 0.132 | 3.194 | 0.088 | 0.174 | 1.584 |
| tetrahydrofuran | 0.118 | 2.769 | 0.562 | 0.206 | 1.703 |
| tetrahydrofuran | 0.178 | 3.008 | 0.373 | 0.227 | 1.543 |
| tetrahydrofuran | 0.183 | 3.078 | 0.375 | 0.219 | 1.656 |
| tetrahydrofuran | 0.181 | 2.887 | 0.303 | 0.212 | 1.457 |
| tetrahydrofuran | 0.186 | 3.163 | 0.333 | 0.186 | 1.587 |
| tetrahydrofuran | 0.159 | 2.780 | 0.541 | 0.209 | 1.471 |
| tetrahydrofuran | 0.175 | 3.274 | 0.825 | 0.194 | 1.553 |
| tetrahydrofuran | 0.141 | 2.997 | 0.457 | 0.206 | 1.580 |
| tetrahydrofuran | 0.176 | 2.792 | 0.232 | 0.201 | 1.394 |
| tetrahydrofuran | 0.190 | 2.691 | 0.335 | 0.219 | 1.455 |
| ethyl acetate | 0.393 | 4.572 | 0.759 | 0.424 | 2.949 |
| ethyl acetate | 0.412 | 4.550 | 0.760 | 0.429 | 2.955 |
| ethyl acetate | 0.391 | 4.547 | 0.843 | 0.413 | 3.121 |
| ethyl acetate | 0.388 | 4.502 | 0.900 | 0.406 | 3.129 |
| ethyl acetate | 0.416 | 4.502 | 0.879 | 0.427 | 3.214 |
| ethyl acetate | 0.392 | 4.690 | 0.669 | 0.407 | 2.938 |
| ethyl acetate | 0.396 | 4.506 | 0.498 | 0.456 | 3.250 |
| ethyl acetate | 0.393 | 4.564 | 1.072 | 0.385 | 3.441 |
| ethyl acetate | 0.373 | 4.533 | 0.759 | 0.413 | 2.983 |
| ethyl acetate | 0.375 | 4.523 | 0.901 | 0.405 | 3.135 |
| ethyl acetate | 0.396 | 4.503 | 0.823 | 0.409 | 3.005 |
| ethyl acetate | 0.391 | 4.600 | 0.769 | 0.418 | 2.819 |
| ethyl acetate | 0.407 | 4.691 | 0.589 | 0.424 | 3.352 |
| ethyl acetate | 0.403 | 4.746 | 1.092 | 0.387 | 3.735 |
| ethyl acetate | 0.409 | 4.629 | -0.025 | 0.403 | 3.102 |
| acetone | 0.139 | 3.621 | 0.510 | 0.227 | 1.873 |
| acetone | 0.186 | 3.497 | 0.280 | 0.250 | 1.587 |
| acetone | 0.210 | 3.212 | 0.407 | 0.246 | 1.617 |
| acetone | 0.220 | 3.677 | 0.067 | 0.246 | 1.690 |
| acetone | 0.194 | 3.309 | 0.457 | 0.251 | 1.697 |
| acetone | 0.200 | 3.294 | 0.495 | 0.221 | 1.574 |
| acetone | 0.189 | 3.293 | 0.560 | 0.221 | 1.819 |
| acetone | 0.213 | 3.506 | 0.399 | 0.247 | 1.804 |
| acetone | 0.165 | 2.730 | 0.325 | 0.216 | 1.449 |
| acetone | 0.181 | 3.384 | 0.430 | 0.237 | 1.679 |
| acetone | 0.193 | 3.272 | 0.323 | 0.228 | 1.545 |
| acetone | 0.192 | 3.216 | 0.356 | 0.234 | 1.570 |
| acetone | 0.211 | 3.834 | 0.411 | 0.242 | 2.036 |

| | | | | | |
|---|---|---|---|---|---|
| acetone | 0.194 | 2.811 | -0.189 | 0.189 | 2.091 |
| acetone | 0.180 | 3.481 | 0.654 | 0.259 | 2.104 |
| ethanol | 0.303 | 1.473 | 0.434 | 0.224 | 1.146 |
| ethanol | 0.312 | 1.721 | 0.478 | 0.233 | 1.337 |
| ethanol | 0.312 | 1.510 | 1.091 | 0.188 | 1.279 |
| ethanol | 0.311 | 1.549 | -0.141 | 0.234 | 0.823 |
| ethanol | 0.280 | 1.554 | 0.154 | 0.215 | 1.228 |
| ethanol | 0.294 | 1.601 | 0.369 | 0.220 | 1.112 |
| ethanol | 0.315 | 1.622 | 0.244 | 0.227 | 1.490 |
| ethanol | 0.307 | 1.546 | 0.331 | 0.208 | 1.602 |
| ethanol | 0.310 | 1.580 | 0.158 | 0.209 | 1.556 |
| ethanol | 0.279 | 1.687 | 0.884 | 0.214 | 1.432 |
| ethanol | 0.292 | 1.595 | 0.471 | 0.222 | 1.211 |
| ethanol | 0.280 | 1.589 | 0.215 | 0.234 | 1.216 |
| ethanol | 0.292 | 1.467 | 0.419 | 0.225 | 1.079 |
| ethanol | 0.351 | 1.537 | 0.358 | 0.223 | 1.140 |
| ethanol | 0.348 | 1.532 | 0.706 | 0.239 | 1.226 |
| methanol | 0.582 | 1.588 | 0.568 | 0.370 | 1.213 |
| methanol | 0.518 | 1.557 | 0.526 | 0.333 | 1.196 |
| methanol | 0.531 | 1.545 | 0.582 | 0.341 | 1.146 |
| methanol | 0.524 | 1.551 | 0.559 | 0.330 | 1.116 |
| methanol | 0.536 | 1.494 | 0.458 | 0.330 | 1.261 |
| methanol | 0.542 | 1.521 | 0.629 | 0.332 | 1.121 |
| methanol | 0.495 | 1.570 | 0.557 | 0.309 | 1.141 |
| methanol | 0.524 | 1.551 | 0.572 | 0.328 | 1.208 |
| methanol | 0.542 | 1.465 | 0.514 | 0.345 | 1.271 |
| methanol | 0.493 | 1.482 | 0.548 | 0.320 | 1.128 |
| methanol | 0.469 | 1.534 | 0.304 | 0.301 | 1.125 |
| methanol | 0.550 | 1.484 | 0.646 | 0.345 | 1.334 |
| methanol | 0.509 | 1.498 | 0.402 | 0.329 | 1.500 |
| methanol | 0.497 | 1.597 | 0.602 | 0.335 | 0.880 |
| methanol | 0.519 | 1.484 | 0.698 | 0.395 | 1.080 |